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Prioritetspåstande fortsat

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Danish Patent Application

Title: Polymer Electrolyte Membrane Fuel Cells

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5

Abstract

10

A method for fabricating gas diffusion electrodes and membrane-electrode assemblies is provided for a high temperature polymer membrane electrolyte fuel cell. With the thermally resistant polymer, e.g., polybenzimidazole (PBI) as binder, the carbon-supported noble metal catalyst is tape-cast onto a hydrophobic supporting substrate. When doped with an acid mixture, electrodes are assembled with an acid doped polymer membrane by hot-press. The fuel cell operates at temperatures up to 200°C with hydrogen-rich fuel containing at least 3 vol% carbon monoxide, compared to the carbon monoxide tolerance of 10-20 ppm level for the Nafion-based polymer electrolyte fuel cell.

15

BACKGROUND OF THE INVENTION

1. TECHNICAL FIELD

5 The present invention is directed to fabrication of gas diffusion electrodes and membrane-electrode assemblies for a high temperature polymer membrane electrolyte fuel cell. The fuel cell operates at temperatures up to 200°C with hydrogen fuel containing at least 3 vol% carbon monoxide.

10 2. BACKGROUND OF THE INVENTION

In operation of a polymer electrolyte fuel cell an oxygen-containing gas is fed to the cathode and a fuel-containing gas (e.g. hydrogen or methanol) to the anode. Hydrogen (or methanol) in the anode feed gas is then electrochemically oxidized by oxygen, forming
15 water (and carbon dioxide) and generating electricity.

The currently well developed technology of polymer electrolyte fuel cells is based on perfluorosulfonic acid polymer membranes (e.g. Nafion®) as electrolyte. The conductivity of this polymer membrane is dependent on the presence of water to solvate the protons
20 from the sulfonic acid groups. Consequently the operational temperature is limited to be below 100°C, typically 60-95°C, at atmospheric pressure.

This is unfortunate because the use of a polymer electrolyte membrane at temperatures higher than 100°C is desirable in several ways. The electrode kinetics will be enhanced and
25 the catalytic activity will be increased at higher temperatures for both electrodes. Another benefit is the reduced poisoning effect of the catalysts by fuel impurities e.g. carbon monoxide, which have been known to be very temperature-dependent, since CO adsorption is less pronounced with increasing temperature. At 80°C, the typical operational temperature of a Nafion-based polymer membrane electrolyte fuel cell, for example, the CO
30 content as low as 20-50 ppm in fuel steam will result in a significant loss in the cell performance. As a consequence very pure hydrogen is needed for operation of polymer electrolyte fuel cells.

For applications as a power system for automobiles, the direct usage of pure hydrogen
35 eliminates the need to develop reliable on-board chemical processors; however, it faces other hurdles such as compact and light-weight fuel storage and network for fuel supply and distribution. Instead of pure hydrogen, liquid fuels such as methanol and gasoline/naphtha are the most favorable fuel for automobile applications. Methanol, among others, is for the time being produced in large quantities and is more easily reformed. Although the
40 infrastructure for supply of methanol to the car fleet needs to be evaluated, it is believed that the development of a methanol infrastructure can be more easily obtained than a hydrogen infrastructure.

On-board processing of these high energy density fuels is also an attractive option to attain
45 high vehicle range and short refueling time. For this purpose an on-board fuel processing

system is necessary in order to convert the fuel into free hydrogen. During the on-board steam reforming carbon in the fuel is converted into carbon monoxide by oxidation with oxygen from the supplied steam, and hydrogen both from the fuel and from the steam is released as free hydrogen. The reformat gas contains therefore hydrogen, carbon dioxide, carbon monoxide, and the residual water and methanol as well. Due to the above-mentioned CO poisoning effect, further purification of the reformat gas is necessary in order to remove CO down to 10 ppm level. This is carried out by means of a water-gas shift reactor, followed by a preferential oxidizer and/or a membrane separator.

For a small dynamic load as in a vehicle, the main challenge for the on-board processing system is the complexity, which not only requires increased cost, size and volume, but also reduces the start-up time and transient response capacity of the system. Such a fuel processing system generally covers 40-50% cost of the fuel cell power stack. This can be decisively simplified by introducing a CO tolerant polymer membrane electrolyte fuel cell.

Direct usage of methanol will be the ultimate option, since the dispensation with the complicated gas processors for reforming and CO removal is very much desired especially for automobile applications. However the technology is far from satisfaction. One of the major challenges is the anodic catalyst. Although Pt/Ru alloy is still recognized as the best, it is not sufficiently active, resulting in high anodic overpotential loss (ca. 350 mV compared to ca. 50 mV for hydrogen) and requiring high catalyst loading of electrode (3.0-8.0 mg/cm²). The insufficient activity of the anode catalyst is due to the slow kinetics of methanol oxidation and the strong poisoning effect of the intermediate species (CO) from methanol oxidation, both expected to be considerably improved by increasing the operational temperature of DMFC.

The newest technology in the field is based on polybenzimidazoles (PBI, Celazole from Hoechst Celanese). US patent No. 5,091,087, for example, discloses a process for preparing a microporous PBI membrane. Being sulfonated (see *US patent 4,814,399*), phosphonated (see *US patent 5,599,639*) or doped with a strong acid (see *US patent 5,525,436* and *Journal of Electrochemical society Vol.142 (1995), L21-L23*), the polymer membrane becomes a proton conductor at temperatures up to 200°C. *US patent 5,716,727* discloses another method for casting the polymer electrolyte membranes directly from an acid solution. It has been shown that this polymer electrolyte membrane exhibits high electrical conductivity (*Journal of Electrochemical society Vol.142 (1995), L21-L23*), low methanol crossover rate (*Journal of Electrochemical Society, Vol.143 (1996), 1233-1239*), excellent thermal stability (*Journal of Electrochemical Society, Vol.143(1996), 1225-1232*), nearly zero water drag coefficient (*Journal of Electrochemical Society, Vol.143(1996), 1260-1263*), and enhanced activity for oxygen reduction (*Journal of Electrochemical Society, Vol.144(1997), 2973-2982*).

It has been suggested that this polymer membrane be used as electrolyte for fuel cells with various types of fuel such as hydrogen (*Electrochemical Acta, Vol.41 (1996), 193-197*), methanol (*Journal of Applied Electrochemistry Vol.26(1996), 751-756*), trimethoxymethane (*Electrochimica Acta Vol.43(1998), 3821-3828*), and formic acid

(*Journal of Electrochemical Society*, Vol.143 (1996), L158-L160). Besides these, this polymer electrolyte membrane has also been used for hydrogen sensors (*Journal of Electrochemical Society*, Vol.144 (1997), L95-L97), electrochemical capacitor and other electrochemical cells (see for example *US patent 5,688,613*).

5 In addition to the acid-doped polybenzimidazole membrane electrolyte, high performance gas diffusion electrodes are also key components for high temperature polymer membrane electrolyte fuel cells. However, little effort has been made so far in this area, compared with
10 other types of fuel cells such as phosphoric acid fuel cells or Nafion-based polymer membrane electrolyte fuel cells. In the above-mentioned patents about the acid-doped PBI electrolyte fuel cells, little information about the manufacturing of gas diffusion electrodes has been included. There are some indications that those workers use phosphoric acid fuel cell electrodes. For example, Wang et al. used phosphoric acid fuel cell electrodes, produced by E-TEK (*Electrochimica. Acta*, vol.41, (1996), 193-197), further treated by
15 impregnation with the polymers. The authors have also made their own electrodes from platinum black, with a very high loading of platinum catalyst (2 mg/cm²). In another publication, Wang et al. use platinum black (Johnson Matthey) and platinum-ruthenium alloy (Giner Inc.) for manufacturing cathode and anode by a filtering-pressing method, also with a very high loading of noble metal catalysts (4 mg/cm²) (*Journal of Applied Electrochemistry* Vol.26(1996), 751-756).
20

3. SUMMARY OF THE INVENTION

25 The present invention provides methods for preparing gas diffusion electrodes and membrane-electrode assemblies for polymer electrolyte fuel cells operating at temperatures up to 200°C. Gas diffusion electrodes were prepared by a tape-casting method with the polymer as binder. The gas diffusion electrode is then doped with a mixture of a nonvolatile acid and a volatile acid. The membrane-electrode assemblies were then fabricated by hot-pressing the doped electrode onto the acid-doped polymer membrane. The assemblies
30 prepared in this way give good performance and high tolerance to the fuel impurities e.g., carbon monoxide.

4. BRIEF DESCRIPTION OF THE DRAWINGS

35 FIG.1. Electric conductivity of PBI membranes as a function of doping level at different temperatures. Measurements were performed at a relative humidity between 61-78%.

FIG.2. Tensile stress of PBI membranes as a function of the doping level at different temperatures.

40 FIG.3. Cell voltage versus current density curves of the high temperature polymer membrane electrolyte fuel cell at different temperatures. Electrodes with a platinum loading of 0.45 mg/cm²; the PBI membrane at doping level of 6.5/1; oxygen at 1 atm and 200 ml/min; and hydrogen at 1 atm and 160 ml/min.
45

FIG.4. Power output of the high temperature polymer membrane electrolyte fuel cell at different temperatures. Electrodes with a platinum loading of 0.45 mg/cm²; the PBI membrane at doping level of 6.5/1; oxygen at 1 atm and 200 ml/min; and hydrogen at 1 atm and 160 ml/min. No humidification for either hydrogen or oxygen.

FIG.5. Cell voltage versus current density curves of the high temperature polymer membrane electrolyte fuel cell at 190°C. Cathode with platinum catalyst of 0.45 mg/cm² and anode with platinum-ruthenium (atomic ratio 1:1) alloy catalyst of 0.45 mg/cm²; the PBI membrane at doping level of 6.5/1; oxygen at 1 atm and 200 ml/min; and hydrogen containing 0 and 3 vol% CO at 1 atm and 160 ml/min. No humidification for oxygen but hydrogen containing CO is humidified by bubbling through a water bath at room temperature.

5. DETAILED DESCRIPTION OF THE INVENTION

The invention relates to methods for preparing gas diffusion electrodes and membrane-electrode assemblies for high temperature polymer membrane fuel cells. The high temperature polymer membrane has been prepared by a solution casting method and thereafter doped with an acid. The fuel cell based on this technology operates at temperatures up to 200°C and tolerates up to at least 3 vol% carbon monoxide in the fuel stream, so that hydrogen-rich gas from a fuel reformer as well as methanol can directly be used for generation of electricity.

For operation of fuel cells the state-of-the-art gas diffusion electrode is such that it provides a complicated interface between a gaseous reactant, a heterogeneous electrocatalyst, and an electrolyte. Two types of electric pathways are provided in this three-phase interface, i.e., an ionic conduction through the electrolyte and an electronic conduction through the supporting substrate. Improving the utilization of noble metal catalysts can only be achieved by optimizing the microstructure of the three-phase interface, since only catalyst particulate siting at the three-phase interface is electrochemically active. Technically this three-phase interface is achieved by constructing the gas diffusion electrode with a hydrophobic polymer and catalyzed carbon powder.

The hydrophobic polymer used in this invention is fluorinated hydrocarbon polymers such as fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE). Fibrous carbon materials in form of paper or cloth are used as the backing materials. By loading a hydrophobic polymer at a high level this backing is permeable to gas reactants. Onto this hydrophobic backing a layer of carbon black containing a lower level of a hydrophobic polymer is prepared. This layer comprises a mass of tiny supporting particles with small pores. The supporting particles can be free from any noble metal catalysts or with a small amount of catalysts. The supported catalyst, prepared by chemical reduction of noble metal ions on carbon supporting materials, is mixed with a soluble polymer. This polymer becomes proton-conductive when doped with a nonvolatile solvent. The slurry is then applied onto the supporting layer. It will wet the supporting layer and partly penetrate into the structure. In this way, the supported catalyst is in good contact with the proton-conductive polymer as well as with the gas-accessible supporting particles.

Polymer membrane electrolytes. The selected polymers include those containing basic groups that can form a single-phase electrolyte with thermally stable acids for application in a solid polymer electrolyte membrane fuel cell. Examples of such polymers are polybenzimidazoles and related families (see e.g., US patents No 4,814,399 and No 5,525,436). The most preferred is polybenzimidazole (PBI, Celazole®), i.e., the poly 2,2'-(m-phenylene)-5,5'-bibenzimidazole product, provided by Celanese Acetate. The polymer has a glass transition temperature of 425-436°C. The polymer powder (-100 mesh) was first mixed with dimethylacetamide (DMAc) and contained in a stainless steel bomb reactor. Lithium chloride was added as a stabilizer. Oxygen was excluded from the bomb by bubbling argon through the mixture solution. The bomb reactor was then closed and placed in a rotating oven at 250°C for 3-5 hours. The solution was then diluted for the membrane casting.

A certain amount of the solution was poured into a glass dish, as described by Fekete et al. (*Polymer Bulletin*, vol.39 (1997), 93-99). The majority of the solvent was evaporated in a ventilated oven at 80-120°C in about 50 hours. The membranes were washed with distilled water at 80°C to remove the residual solvent and stabilizing salts.

The membranes obtained in this way were doped with a acid of various concentrations. The acid can be phosphoric acid or sulfuric acid. Doping levels, defined as the molar ratio of the doping acid to PBI (repeating unit), depend on the concentration of the acid, temperature, and duration. With high doping levels, the membranes exhibit high electric conductivity but low mechanical strength (See Figs. 1 and 2). A proper doping level between 4.5 and 7.0 is preferred, corresponding to an electric conductivity of 0.03-0.05 S/cm and a tensile stress of 180-380 kg/cm² at temperatures around 150°C.

Carbon-supported noble metal catalysts

Chloroacids of noble metals from Group VIII of the periodic table, particularly platinum and ruthenium, were first prepared. Different types of carbon black of high surface area (typically from 200 to 1000 m²/g), either graphited or non-graphited, can be used as supporting materials. With help of a surface agent, e.g., acetic acid, the metal ions were chemically reduced by a reducing agent selected from, among others, formic acid, formaldehyde, sodium borohydride, etc. The obtained carbon supported catalyst was then filtered and washed with distilled water and dried and ground into fine powder. Alloying of metals can be prepared by using a mixture solution of desirable metal chloroacids.

Gas diffusion electrodes

Various fibrous carbon materials in form of paper or cloth can be used as the backing substrate. It is generally desirable that the materials have low electric resistance in the operational temperature range of a fuel cell. For convenience of tape-casting, carbon fibrous paper, for instance, Toray TGP-H-120, was preferred. The carbon material was first wet-proofed by immersing in a hydrophobic polymer dispersion, such as fluorinated ethylene

propylene or polytetrafluoroethylene, and then dried and sintered at 360°C for 20 minutes. The loading of the hydrophobic polymer is controlled by changing concentration of the dispersion.

- 5 A slurry of uncatalyzed carbon powder with 40% PTFE was prepared and applied on to the hydrophobic backing substrate carbon paper to form a supporting layer. After sintering at 360°C for 20 minutes, this layer is hydrophobic. In addition, this layer provides a smooth surface of tiny particles and therefore prevents the catalyst layer from cracking.
- 10 Carbon supported noble metal catalyst, with a weight ratio of the noble metal to carbon from 0.1 to 0.2, were mixed with a soluble polymer, i.e., polybenzimidazole solution in dimethylacetamide, and applied to the top of the supporting layer on a wet-proofed carbon paper. The electrodes were then dried and sintered at 130 - 190°C for 30 - 180 minutes. The concentration of the PBI solution is of importance for the fluidity of the slurry. The loading
- 15 of PBI in the catalyst layer of electrodes is preferably around 0.5 - 1.5 mg/cm². The electrodes made in this way have a platinum loading of 0.2 - 0.8 mg/cm².

Membrane-electrode assemblies

- 20 The catalyst layer in the gas diffusion electrodes, as described above, contains the PBI polymer component. This polymer needs to be doped with an acid in order to achieve the protonic conductivity. This is done with a mixture of a nonvolatile acid and a volatile acid. The nonvolatile acid is the same acid as used for doping the membrane, i.e., either sulfuric acid or phosphoric acid. The volatile acid, e.g., trifluoroacetic acid or acetic acid, is used to
- 25 facilitate the wetting of the dopant solution on the surface of the electrode. The amount of the nonvolatile acid used for doping is critical since excessive acid will reduce the membrane strength when the membrane-electrode assembly is made by means of hot-press. This amount is determined by the polymer content in the catalyst layer of electrodes. A molar ratio of the nonvolatile acid to the polymer content is preferred in a range from 5/1 to
- 30 20/1, and preferably from 10/1 to 15/1.

- Assemblies from the doped electrodes and the doped polymer membranes were made by means of hot-press. Temperature, pressure and duration are critical parameters and a set of optimal parameters are found to be temperature 130-200°C, pressures of 0.3-1.0 bar/cm²,
- 35 and a duration of 5-30 minutes.

Single cell tests and carbon monoxide tolerance

- 40 A single test cell (5 cm²) has been built up to perform electrochemical characterizations of the membrane-electrode assemblies. Graphite plates with gas channels were used as the holder. Two aluminium end plates with attached heaters are used to clamp the graphite plates and collect current. Temperature is controlled by a controller. Fuel and oxidant gases were supplied by means of mass flow controllers. Performance curves were obtained by the current step potentiometry. Potential values at various current densities were then taken from
- 45 chronopotentiometric curves when a steady state was reached.

5 It is well known that the Nafion-based membrane electrolyte usually has a large electro-osmotic drag number, i.e., water moves from the anode side to the cathode side during cell operation, resulting in the requirement of an intensive gas humidification to maintain an adequate membrane hydration. This, together with operational temperatures near the boiling point of water, makes the cell operation very critical with respect to both water and heat management.

10 As a consequence of the reported nearly zero water drag coefficient of the high temperature polymer membranes, the fuel cell based on PBI membrane can operate with no humidification of the reactive gases, i.e., the internally formed water is enough to maintain the polymer membrane electrolyte. The elimination of humidification substantially simplifies the construction and operation of the polymer fuel cell.

15 For evaluating the tolerance of the technology to fuel impurities, a mixture of 97 vol% hydrogen and 3 vol% carbon monoxide was pre-made. Mixed gas of other compositions was obtained by means of mass flow meters and controllers (Bronkhorst, HI-TEC E-5514). It is found that the present technology can tolerate up to at least 3 vol% carbon monoxide in the hydrogen fuel, i.e., 20,000-30,000 ppm CO compared to 10-20 ppm CO for Nafion-based
20 polymer electrolyte fuel cells.

The poisoning effect of platinum catalysts by carbon monoxide has been intensively studied by many investigators in the field of fuel cells and electrocatalysts (*see for example J. Electrochem. Soc.*, 133, 1574 (1986), and *J. Electrochem. Soc.*, 134, 3021 (1987)). These
25 studies have mainly been concentrated on the mechanism of adsorption and oxidation and the nature of the absorbed species on the noble metal electrodes in various acid electrolytes. Two kinds of adsorption mechanisms have been proposed, i.e. the linearly and bridge or multi-bonded CO species. As assumed, the linearly absorbed carbon monoxide species, $-\text{CO}$, involve one adsorption site per CO particle, whilst the bridge or multi-bonded carbon
30 monoxide species, $=\text{CO}$, require two or more adjacent platinum surface sites. In the case of hydrogen oxidation on a carbon-supported platinum gas-diffusion electrode in the presence of carbon monoxide, the poisoning effect is found to depend on the ratio of carbon monoxide concentration to the hydrogen concentration, $[\text{CO}]/[\text{H}_2]$. This indicates that the poisoning is a simple competition with hydrogen for active sites, since the strong chemisorptive bond of the
35 carbon monoxide molecule may lead to a surface blockage from hydrogen oxidation.

In the present invention, it is found that the poisoning effect of CO is suppressed by the presence of water vapor at temperatures around 200°C. The possible mechanism is the
40 chemical and/or electrochemical oxidation of carbon monoxide at the surface of electrode catalysts, i.e., the water vapor in the CO-containing fuel steam preferably oxidizes carbon monoxide via a water-gas shift reaction with help of the electrode catalysts.

The fact that the high temperature polymer membrane electrolyte fuel cell can tolerate CO
45 2000-3000 times higher than that for Nafion-based polymer electrolyte fuel cells, will decisively simplify or potentially eliminate the CO removal processors from a reforming

system. The resulting power system will therefore be much more compact, light and cost-efficient with enhanced power density and improved transient performance. This is of special importance for automobile applications.

5 EXAMPLE 1

20 grams of 3 wt% PBI solution in dimethylacetamide were poured into a glass dish of 145 mm diameter. After drying in a ventilated oven at 85°C for 30 hours, 100°C for 10 hours, and then at 120°C for 10 hours, the polymer membrane were washed with distilled water at 10 80°C to remove the residual solvent and stabilizing salts.

The membrane was thereafter immersed in phosphoric acid of concentration 50, 65, 75, and 90 wt%, respectively. After 15 days at room temperature, the membrane was doped at levels of 3.1, 6.5, 9.8, and 16.1, accordingly. Figure 1 shows the conductivity of the 15 membrane as a function of the doping level at temperatures of 25 and 150°C, respectively. Figure 2 shows the tensile stress of the membrane as a function of the doping level at temperatures of 25 and 150°C, respectively.

20 EXAMPLE 2

On to the wet-proofed carbon backing substrate (Toray paper TGP-H-120, Toray Ind. Inc.) a slurry of 60 wt% carbon powder (Vulcan XC-72, Cabot) and 40 wt% polytetrafluoroethylene (PTFE) was applied. The resulting layer was then dried and sintered at 370°C for 20 minutes. This supporting layer is hydrophobic so that it allows access of 25 reactive gases. As a bridge between the carbon paper backing and the catalyst layer this layer prevents also the electrode from serious cracking after drying and sintering.

The platinum chloroacid was first prepared by dissolution of metallic platinum in a mixture of concentrated nitric acid and hydrochloride acid. The platinum chloroacid was then mixed 30 with carbon powder (Vulcan XC-72, Cabot). With help of surface active agents the noble metal was chemically reduced on the surface of the carbon powder at 95°C. The obtained carbon-supported platinum catalyst (20 wt% Pt) was then filtered, washed with distilled water, dried, and finally ground into fine powder.

35 A mixture of 40 wt% Pt/C catalyst powder and 60 wt% PBI from a 3 wt% polymer solution in dimethylacetamide was well mixed and applied on to the supporting layer of the carbon paper by tape-casting. The platinum loading in the catalyst layer is 0.45 mg/cm². After drying at 130°C for 10 minutes, the electrode was impregnated with a mixed acid of 65 wt% phosphoric acid and 35 wt% trifluoroacetic acid. The amount of impregnated 40 phosphoric acid is related to the PBI content in the catalyst layer of the electrode, in a molar ratio of 14 to 1.

From the impregnated electrodes and acid-doped PBI membranes (doping level 6.5), a 45 membrane-electrode assembly was made by means of hot-press at a temperature of 150°C, a pressure of 0.5 bar/cm², and a duration of 12 minutes. The assembly was then placed in a

test cell. Current density versus cell voltage curves at each test temperature were measured after the cell performance reached a steady state. Both hydrogen and oxygen were under atmospheric pressure. Fig. 3 shows the performance curves at temperatures 150, 170, and 190°C, respectively. Fig. 4 shows the power output of the test cell as a function of current density at temperatures 150, 170, and 190°C, respectively.

EXAMPLE 3

On to the wet-proofed carbon substrate (Toray paper TGP-H-120, Toray Ind. Inc.) a slurry of 60 wt% carbon powder (Vulcan XC-72, Cabot) and 40 wt% PTFE was applied and then dried and sintered at 370°C for 20 minutes.

Platinum chloroacid was first prepared by dissolution of metallic platinum in a mixture of concentrated nitric acid and hydrochloride acid. Ruthenium chloride (hydrated) was provided by Aldrich. A mixture of platinum chloride and ruthenium chloride of the metal atom ratio 1:1 was slurried with carbon powder (Vulcan XC-72, Cabot) and chemically reduced at 95°C. The Pt-Ru/C catalyst was filtered, washed with distilled water, dried, and finally ground into fine powder.

A mixture of 45 wt% Pt/C catalyst powder and 55 wt% PBI from a 2 wt% solution in dimethylacetamide was prepared and applied on to the supporting layer of the carbon substrate, as the cathode. A mixture of 45 wt% Pt-Ru/C catalyst powder and 55 wt% PBI from a 2 wt% solution in dimethylacetamide was prepared and applied on to the supporting layer of the carbon substrate, as the anode. The platinum loading in the catalyst layer of both electrodes was 0.45 mg/cm². After drying at 130°C for 5 minutes, the electrode was impregnated with a mixed acid of 60 wt% phosphoric acid and 40 wt% trifluoroacetic acid. The amount of impregnated phosphoric acid was related to the PBI content in the catalyst layer of the electrode, being in a molar ratio of 12 to 1.

From the impregnated electrodes and acid-doped PBI membranes (doping level 6.5), a membrane-electrode assembly was made by means of hot-press at a temperature of 150°C, a pressure of 0.4 bar/cm², and a duration of 15 minutes. The assembly was then placed in a test cell. Cell voltage versus current density curves at each measuring temperature were measured after the cell performance reached a steady state. Pure hydrogen and hydrogen containing 1 to 3 vol% CO were used as the fuel gas. Both hydrogen-containing fuel and oxygen are under atmospheric pressure. Fig. 5 shows the performance curves at 190°C for hydrogen containing 0, 1, and 3 vol% carbon monoxide.

Although this invention has been shown and described with respect to detailed embodiments hereof, it will be understood by those skilled in the art that many variations and modifications in form and detail thereof may be made without departing from the spirit and scope of the claimed invention. Therefore we claim:

1. A method for fabricating gas diffusion electrodes and membrane-electrode assemblies for high temperature polymer membrane electrolyte fuel cells comprising the following steps:

- (A). preparing the carbon supporting substrate by treatment in a hydrophobic polymer solution
- (B). casting a supporting layer from a slurry, said slurry comprising carbon black, a hydrophobic polymer, and a solvent as the temporary binder
- (C). casting a catalyst layer from a slurry, said slurry comprising carbon-supported noble metal catalysts and a selected polymer as binder
- (D). doping the catalyst layer with a mixture of a nonvolatile acid and a volatile acid
- (E). and finally hot-pressing the electrodes onto an acid-doped polymer membrane electrolyte

- 5 2. The high temperature polymer membrane electrolyte fuel cell of claim 1 comprising a gas diffusion cathode for reducing an oxygen-containing oxidant gas, a gas diffusion anode for oxidizing a hydrogen-rich fuel gas, and a solid polymer membrane electrolyte, said polymer electrolyte consisting of an acid-doped polybenzimidazole membrane.
- 10 3. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the hydrogen-rich fuel gas may contain at least 3 vol% carbon monoxide.
- 15 4. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the oxygen-containing gas may operate without humidification while the hydrogen-rich fuel gas needs to be humidified at room temperature.
- 20 5. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion cathode consists of a carbon backing substrate, a hydrophobic carbon supporting layer, and a catalyst layer.
- 25 6. The gas diffusion cathode of claim 5 wherein the hydrophobic carbon supporting layer consists of 40-60 wt% carbon black and 60-40 wt% hydrophobic polymer, fabricated by a tape-casting method and then dried and sintered 360-370°C for 10-15 minutes.
7. The gas diffusion cathode of claim 5 wherein the catalyst layer consists of 30-55 wt% catalyst powder and 70-45 wt% soluble polymer components, fabricated by slurry casting and then dried at temperatures between 130-180°C for 3-15 minutes.
8. The catalyst layer of claim 7 wherein the soluble polymer comprises polybenzimidazole solution in dimethylacetamide.
- 30 9. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion anode has the same structure as the gas diffusion cathode described in claims 3-8,

the said catalyst powder consists of 10-20 wt% platinum-ruthenium alloy and 80-90 wt% carbon black.

- 5 10. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion cathode and anode are doped with a mixture of acids, said acid mixture consisting of 30-70 wt % nonvolatile acid and 30-70 wt% volatile acid.
- 10 11. The dopant acid of claim 10 wherein the nonvolatile acid is phosphoric acid or sulfuric acid and the volatile acid is trifluoroacetic acid or acetic acid.
- 15 12. The dopant acid of claim 11 wherein phosphoric acid is in a concentration range from 5 wt% to 20 wt% and the molar ratio of the acid to the polymer contained in the catalyst layer is from 5 to 20, preferably from 10-15.
- 20 13. The high temperature polymer membrane electrolyte fuel cell of claim 2 wherein the gas diffusion cathode and anode (claims 3-10) and the acid-doped polymer membrane electrolyte are assembled by means of hot-press.
14. The membrane-electrode assemblies of claim 15 wherein the hot-press is performed at a temperature from 130 to 200°C, a pressure from 0.3 to 1.0 bar/cm², and a duration from 8 to 20 minutes.

Modtaget PD

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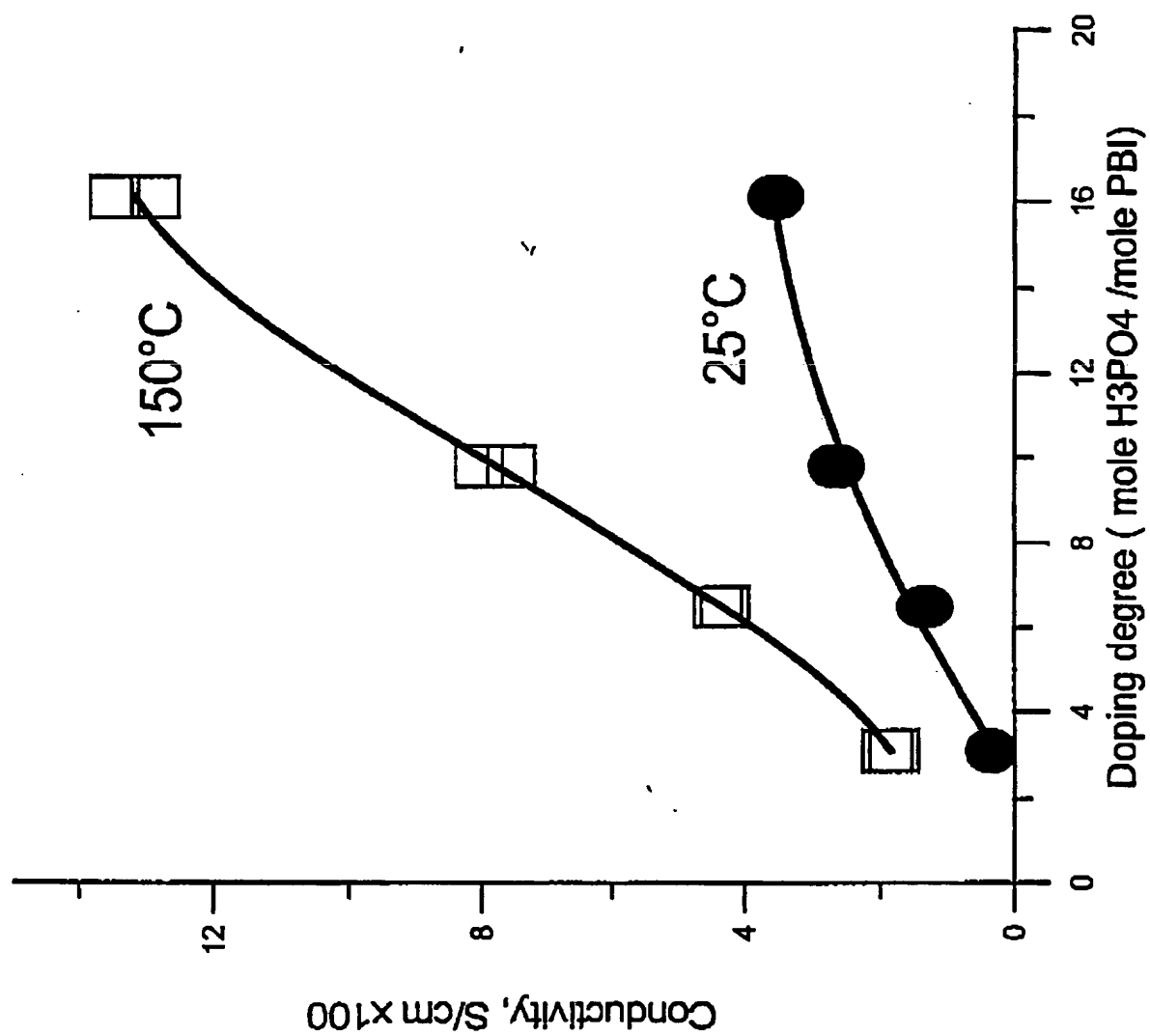


FIG. 1

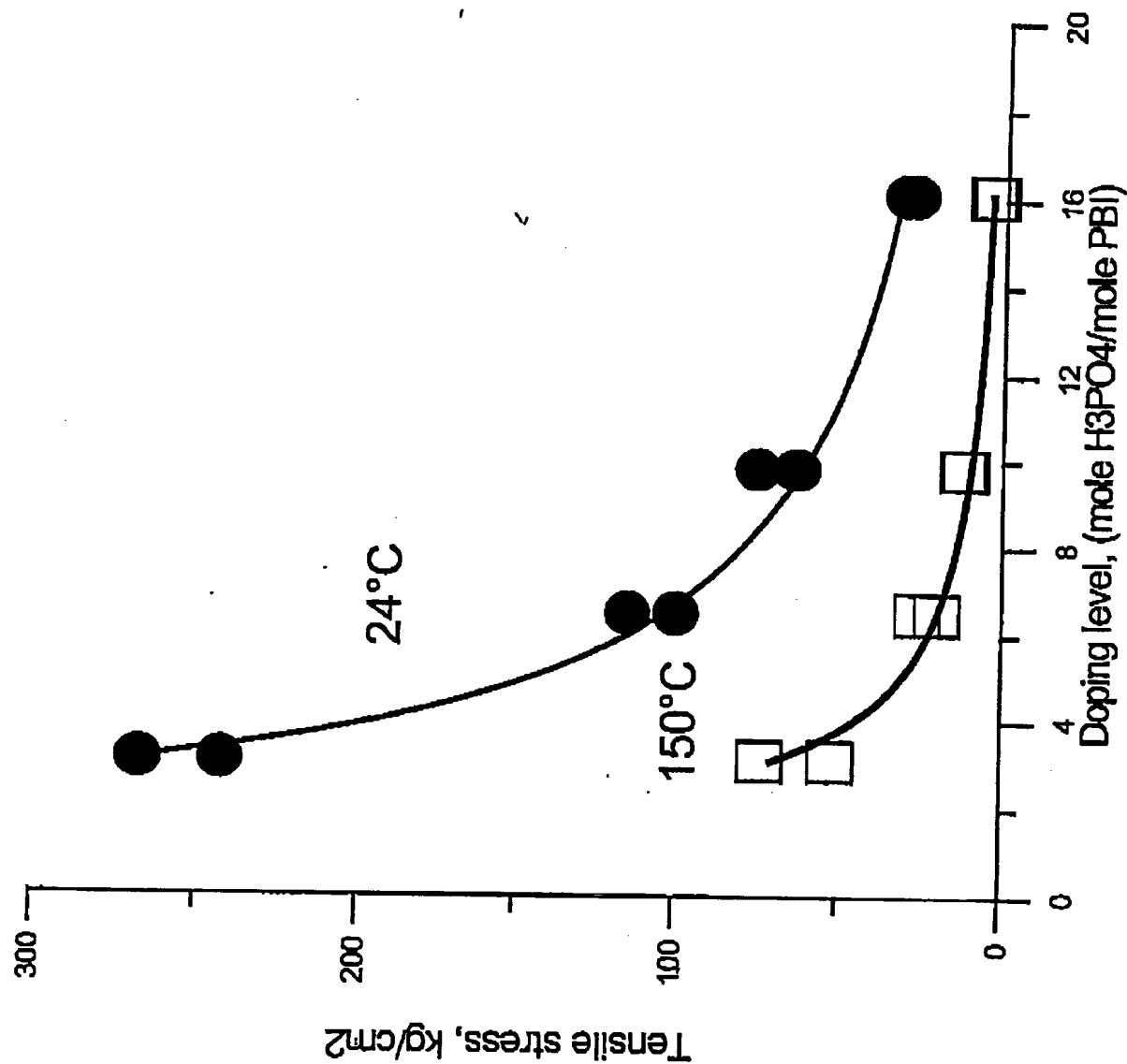


FIG. 2

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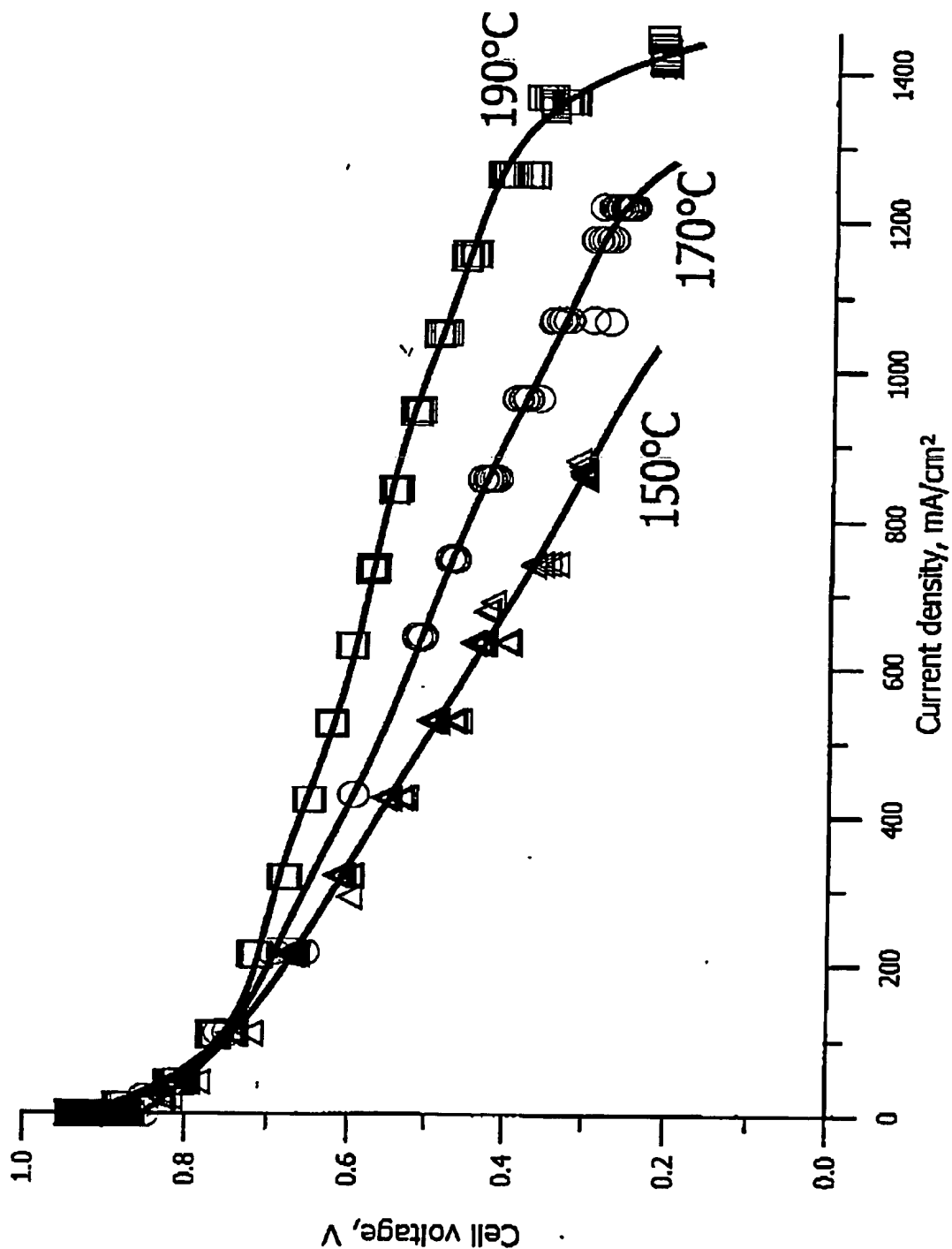


FIG. 3

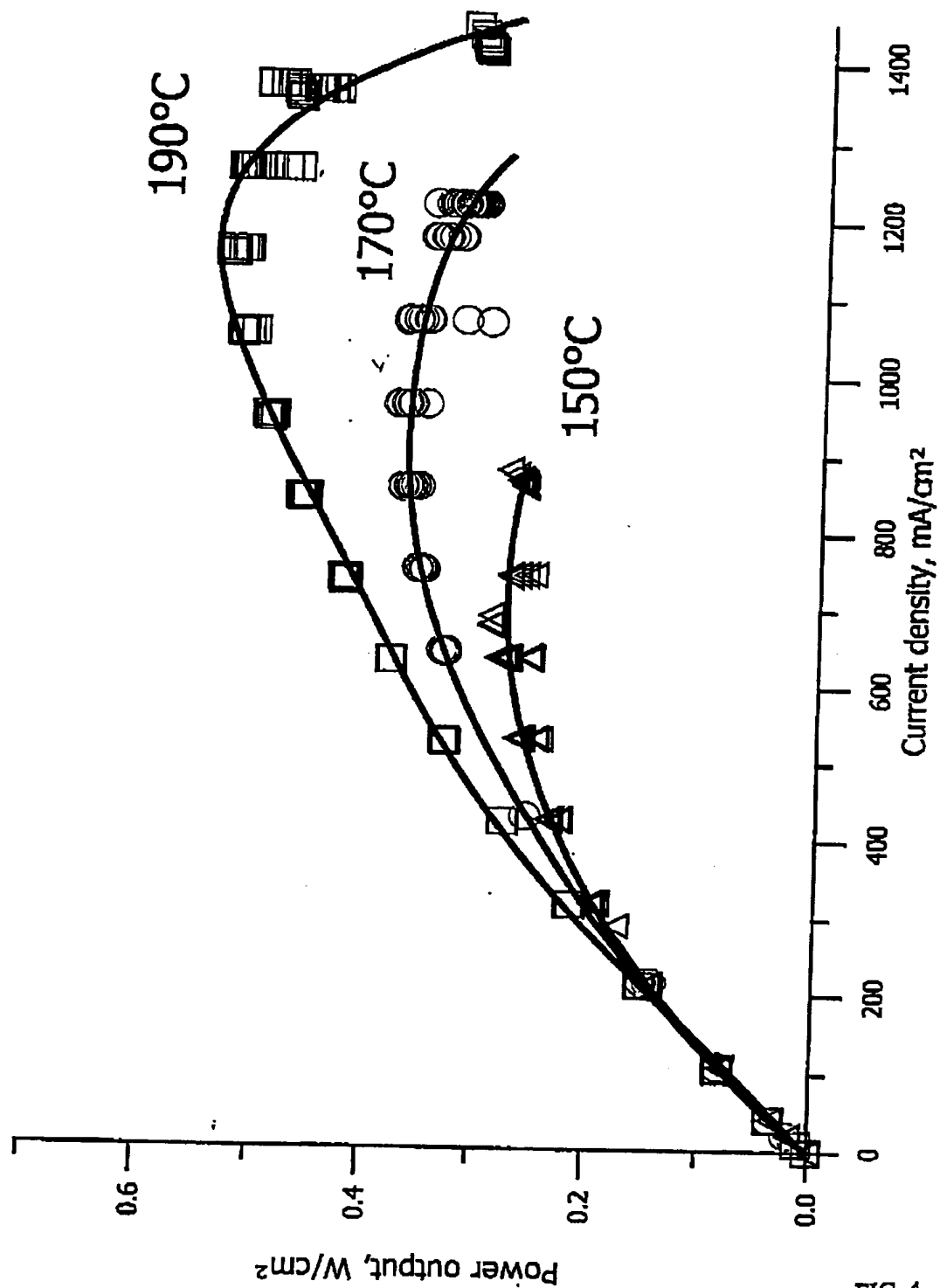


FIG. 4

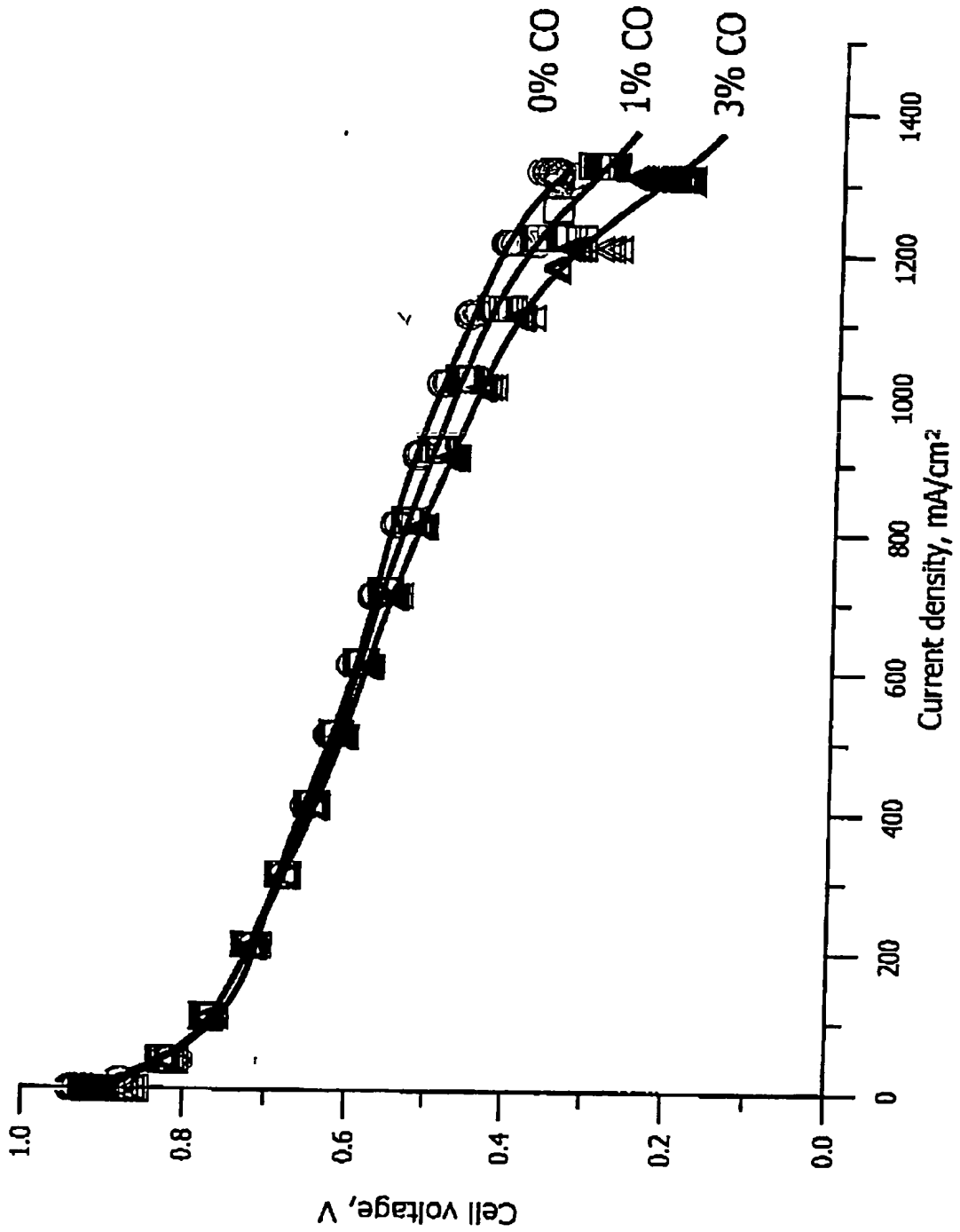


FIG.5

